

# Temperature-Programmed Liquefaction of Coals Using Bimetallic Dispersed Catalysts from Organometallic Complexes

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## Introduction

It has been recognized recently that dispersed catalysts are superior to supported catalysts for primary coal liquefaction. Most previous work involved dispersed molybdenum sulfide from a water-soluble salt [Derbyshire, 1988]. Some organometallic compounds including metal carbonyls and naphthenates have also been tested as catalyst precursors [Suzuki et al., 1987; Herrick et al., 1990; Swanson, 1992], which often requires the addition of sulfur compounds [Yamada et al., 1985]. There are some unique advantages of organometallic compounds as catalyst precursors. First, most organometallic compounds are soluble in hydrocarbon solvents and may be used as oil-soluble precursors. Second, as has been demonstrated by Hirschon and Wilson [1991, 1992], some organometallic compounds can be easily decomposed to metal sulfides at low temperatures. The present work is concerned with organometallic precursors which can directly produce metal sulfides upon thermal decomposition.

Little work on bimetallic dispersed catalyst for coal liquefaction has appeared, although previous work on multicomponent catalysts has involved the mixture of two or more inorganic salts [Garg and Givens, 1984; Song et al., 1986, 1991; Sommerfeld et al., 1992]. Related to this work is a general observation from previous investigations that there could be synergistic effects between different metals, and an organometallic precursor may be better than an inorganic one. Our interest in the heteronuclear organometallic compounds was stimulated by the recent book on metal clusters published by Mingos and Wales [1990]. It seemed to us that highly active catalysts might be prepared from some clusters containing metal-metal bonds, especially the "thiocupane" clusters containing two metals such as Fe or Co and Mo in a single molecule.

Two different metals bound together in a single compound should have a more systematic spatial arrangement in the resulting catalytic phase upon thermal decomposition than if two separate compounds were used to introduce the two different metals to a catalytic system. The present work is an exploratory study of bimetallic dispersed metal sulfide catalysts for coal liquefaction, involving the synthesis of the organometallic thiocupane clusters that contain Mo and Co as well as sulfur in a single molecule, and liquefaction of coal impregnated with the precursors under non-programmed and temperature-programmed (TPL) conditions, where the programmed heat-up serves as a step for both catalyst activation and coal pretreatment or preconversion. The advantages of temperature-programmed conditions have been demonstrated in our recent work [Song et al., 1992; Song and Schobert, 1992; Huang et al., 1992].

## Experimental

### Catalyst Precursors and Coal Samples

Three bimetallic thiocubanes were used as catalytic precursors:  $\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$  [MoCo-TC1],  $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$  [MoCo-TC2], and  $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp}')_2(\text{CO})_2$  [MoCo-TC3], in which Et, Cp and Cp' represent ethyl group, cyclopentadiene, and pentamethylcyclopentadiene, respectively. These thiocubanes were synthesized in our laboratory based on the procedures of Brunner and Watcher [1982] and Halbert et al. [1985]. For comparative examination, bimetallic metal sulfide complex, cobalt bis-tetrathiomolybdate trianion was also synthesized based on the procedure of Pan et al. [1985]. The trianionic compound,  $(\text{PPh}_4)_3\text{Co}(\text{MoS}_4)_2$ , is designated as MoCo-S.

The U.S. Department of Energy Coal Samples (DECS, #9 and #12) were obtained from the Penn State/DOE Coal Sample Bank. The Montana subbituminous coal (DECS-9, PSOC-1546, < 60 mesh) has the following composition: 24.7% moisture, 4.8% ash, 33.5% volatile matter, and 37.1% fixed carbon on an as-received basis; 76.1% carbon, 5.1% hydrogen, 0.9% nitrogen, 0.3% organic sulfur, and 17.5% oxygen on a dmmf basis. The Pittsburgh #8 bituminous coal (DECS-12, PSOC-1549, < 60 mesh) has the following composition: 2.4% moisture, 10.0% ash, 35.2% volatile matter, and 52.4% fixed carbon on an as-received basis; 84.8% carbon, 5.7% hydrogen, 1.4% nitrogen, 0.7% organic sulfur, and 6.5% oxygen on a dmmf basis. The coals were dried for two hours at 100°C in a vacuum oven before use.

### Incipient Wetness Impregnation of Catalyst Precursors

The catalytic precursors were dispersed on to the coal by the incipient wetness impregnation (IWI) method using organic solvents. IWI method was applied to coal in a previous work [Huang et al., 1992]. Because of the difference in the solubility of the organometallic precursors, several solvents including toluene, THF,  $\text{CHCl}_3$  and acetonitrile were used for dissolving them. The organic solution of a precursor was intermittently added dropwise to the dried coal in a 100 mL beaker, in a fashion that the wet spots over the coal particles do not touch each other, followed by manual stirring with a glass rod until all signs of wetness disappeared. In order to keep the metal loading from different precursors at a constant level, we first estimated the incipient wetness volume prior to the catalyst impregnation with a given solvent, which means the total volume of the solvent needed to reach the point of incipient wetness: the point when the solution drops begin to remain on the external surface of the coal. The loading for the bimetallic thiocubanes was 0.5-0.6 wt% of molybdenum on the basis of dmmf coal. The impregnated coal sample was dried at 100°C for 2 h in a vacuum oven. IWI method is often used for loading inorganic salts from their aqueous solution on to a catalyst support without [Solar et al., 1991]. It should be noted that the IWI method used in our work is different from conventional one in that we only use certain amount of solution defined by the estimated incipient wetness volume to achieve a constant metal loading.

### Liquefaction under SSL and TPL Conditions

All reactions were carried out in 25 mL tubing bomb microautoclaves in a temperature-controlled fluidized sandbath. Each reaction used approximately 3 g dried coal. 1-Methylnaphthalene was used as the reaction solvent (3 g) unless otherwise mentioned. In several experiments tetralin was also used as a hydrogen-donor solvent (3 g) for comparison. The initial  $\text{H}_2$  pressure was 7 MPa at room temperature for all the runs. For catalyst screening, single-stage liquefaction (SSL) was performed, where the tubing bomb was rapidly heated to the prescribed temperatures (400-425. °C) for 30 minutes (plus a three minute heat-up period) followed by a rapid quench in cold water bath. Temperature-programmed liquefaction (TPL) had the tubing bomb rapidly heated up to a low temperature (275°C in all the catalytic runs, 200°C in the thermal

runs) and soaked at that temperature for 30 minutes before the temperature was gradually increased (5-7°C/min) to a higher temperature (400°C-425°C) and held there for 30 minutes before rapid quenching with cold water bath. These procedures were established in our recent work [Song and Schobert, 1992; Huang et al., 1992].

The gaseous product was vented after the reaction was complete and the liquid and solid products were washed into a tared ceramic thimble with hexane. The products were separated under a N<sub>2</sub> atmosphere by Soxhlet-extraction using hexane, toluene, and THF in succession. Solvents were removed by rotary evaporation, and the products were dried in vacuum at 100°C for 6 h except for the hexane-solubles. The asphaltene (toluene soluble, but hexane insoluble), preasphaltene (THF soluble, but toluene insoluble), and residue were weighed and the conversion and product distribution were calculated based on dmmf coal. All the runs were repeated at least once or twice to confirm the reproducibility. In most cases, the experimental errors were within  $\pm 2$  wt% for conversion, and the average data are reported here.

## Results and Discussion

### Effects of Precursor Type and Solvents for Impregnation

Table 1 shows the results of liquefaction of the Montana subbituminous coal at 400°C for 30 min. We first prepared and tested Mo<sub>2</sub>Co<sub>2</sub>S<sub>4</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>(CO)<sub>2</sub> [MoCo-TC1], which was first synthesized and used recently by Halbert et al. [1991] in preparing MoCo hydrotreating catalyst. Using MoCo-TC1 impregnated on to DECS-9 coal from acetonitrile, however, showed little catalytic effect for increasing conversion. Replacing CH<sub>3</sub>CN with THF for impregnating MoCo-TC1 increased coal conversion relative to the thermal run by 14 wt%, but did not improve oil formation to any significant extent. It seems that the acetonitrile solution and the dithiocarbamate and acetonitrile ligands in MoCo-TC1 can poison the resulting catalyst under the conditions employed. This observation prompted us to prepare the thiocubane which contains no nitrogen in the ligands, leading to the synthesis of Mo<sub>2</sub>Co<sub>2</sub>S<sub>4</sub>Cp<sub>2</sub>(CO)<sub>2</sub> [MoCo-TC2], and Mo<sub>2</sub>Co<sub>2</sub>S<sub>4</sub>(Cp'')<sub>2</sub>(CO)<sub>2</sub> [MoCo-TC3]. The basic difference between these three thiocubanes is the type of ligands to the Mo [Cp = C<sub>5</sub>H<sub>5</sub>, Cp'' = C<sub>5</sub>Me<sub>5</sub>; all the five (ring) carbon atoms are equidistant from the metal atom].

MoCo-TC2 impregnated from toluene afforded much higher conversion and oil yield; it appears to be much more active than MoCo-TC1. MoCo-TC3 exhibited slightly lower catalytic activity compared to MoCo-TC2. It was expected that MoCo-TC2 would afford greater conversion when THF was used as the impregnating solvent, since THF is a better swelling solvent and can penetrate the coal structure, which would improve the dispersion of the resulting Co-Mo bimetallic sulfide catalyst. Surprisingly, the catalytic liquefaction using MoCo-TC2 gave both higher oil yields and total conversion when toluene was used rather than THF. The structure and ligands of MoCo-TC3 and MoCo-TC2 are of the same nature, except that cyclopentadiene in MoCo-TC2 is substituted by pentamethylcyclopentadiene in MoCo-TC3. There was a small increase in the oil yield coupled with a decrease in preasphaltene yield when MoCo-TC3 was used in temperature-programmed liquefaction. Table 2 presents the results of catalytic runs of DECS-9 coal at 425°C. The order of catalytic activity at 425°C is the same as that observed from runs at 400°C: MoCo-TC2 > MoCo-TC3 > MoCo-TC1.

In an attempt to examine the role of bonding between Co and Mo, we further prepared and tested heterometallic cluster of the form Co(MoS<sub>4</sub>)<sub>2</sub><sup>3-</sup> which has distinctly different structure than the above-mentioned thiocubanes. Comparing results in Table 1 and Table 2 reveal that MoCo-S is more active than MoCo-TC1 at both 400 and 425°C but is much less active compared to MoCo-TC2, regardless of the

impregnating solvent.

Table 3 shows the effect of using the catalytic precursors on liquefaction of DECS-12 Pittsburgh #8 bituminous coal. At 400°C, the catalytic effects appear to be enhanced coal conversion to preasphaltene and asphaltene, with little increase in oil production relative to thermal run. At 425°C, using MoCo-TC2 increased total conversion significantly compared to the thermal run; it also promoted oil production moderately. However, increasing temperature from 400°C to 425°C caused decrease in total conversion both in thermal run and catalytic runs. In both cases, MoCo-TC2 was much more active than MoCo-TC1, although the latter was used under better conditions (TPL) than the former (SSL), as we further describe below. This again points to the negative impact of the  $\text{CH}_3\text{CN}$  and  $\text{S}_2\text{CNEt}_2$  ligands in MoCo-TC1 upon the resulting catalyst in coal liquefaction. Therefore, it appears that an active MoCo bimetallic sulfide catalyst is generated in-situ from MoCo-TC2 during liquefaction. Under comparable conditions the catalyst from MoCo-TC1 is much less active, although an active catalyst could be generated also from this precursor if first decomposed at low temperature followed by venting and purging to remove poisonous compounds and followed by re-charging  $\text{H}_2$  gas and heat-up.

By combining Tables 1, 2 and 3 it becomes very clear that MoCo-TC2 is the best precursor and MoCo-TC1 is the worst precursor among the three thiocubanes which differ from each other only in the type of ligands to Mo. Bimetallic sulfide complex MoCo-S also produces a catalyst whose activity is lower than that from MoCo-TC3 at 400°C and close to MoCo-TC3 at 425°C. In MoCo-S, the Co and Mo are bound through sulfur-bridge bonding, but in MoCo-TC2 or TC3, there are direct metal-metal bonds between Co-Mo, Co-Co, and Mo-Mo in addition to the sulfur-bridges. The superiority of MoCo-TC2 over MoCo-S may suggest the importance of direct metal-metal bonding; the differences between the three thiocubanes clearly indicate the importance of ligand type. The solvents used for loading the precursors are also influential. Both toluene and THF were tested for impregnating MoCo-TC2 but the non-polar solvent seems to be better in terms of higher oil yield; the optimum solvent and method for loading catalyst are not known yet. In summary, the above results indicate that both the ligands to the metal species and the type of bonding between the two metals affect the activity of the resulting bimetallic MoCo sulfide catalyst significantly. For a given precursor, the solvent used for catalyst impregnation also affects coal conversion, although the impregnating solvent was removed before reaction.

### Effects of Temperature-Programming

The second major task in this study is to optimize the performance of promising catalysts selected from screening tests described above. As a means to increase conversion, the liquefaction of coals impregnated with the precursors was carried out under temperature-programmed (TPL) conditions, where the programmed heat-up serves as a step for both catalyst activation (precursor decomposition to active phase) and coal pretreatment or preconversion.

Table 4 shows the effects of temperature-programming on the catalytic and thermal runs of both DECS-9 and DECS-12 coals. In the presence of either MoCo-TC2 or MoCo-TC3, TPL runs in 1-MN always give higher conversions and higher oil yields than the corresponding SSL runs. At a final reaction temperature of 425°C with 1-MN solvent, TPL runs of both DECS-9 and DECS-12 coals using MoCo-TC2 or TC3 gave 13-15 wt% higher conversions and 5-11 wt% higher oil yields than the corresponding SSL runs. Most of the trends observed from Table 4 can be rationalized based on a general reaction model for liquefaction presented in recent papers [Song et al., 1989, 1991].

The first question that arises is why programmed heat-up is better than rapid heat-up? The superiority of TPL over SSL in catalytic runs with 1-MN solvent could be due to 1) more products from coal after longer residence time irrespective of catalyst, since a programmed heat-up is included in TPL but SSL only involves a very rapid heat-up in about three minutes followed by reaction at 400 or 425°C; 2) due to reactions including precursor decomposition and catalytic reactions during programmed heat-up. The first is not the case, as demonstrated by the fact that in the non-catalytic runs in 1-MN, using temperature programmed heat-up had essentially no impact on the liquefaction of DECS-9, neither on total conversion nor on product distribution, as can be seen from Table 4. The desirable effects of TPL, therefore, are associated with low-temperature catalytic hydrogenation reactions during programmed heat-up.

It is interesting to note from Table 4 that under TPL conditions using 1-MN solvent, increasing final temperature of all the catalytic runs from 400 to 425°C further increased coal conversions and oil yields considerably. In distinct contrast, under SSL conditions, increasing temperature of the catalytic runs (using MoCo-TC2, TC3) from 400 to 425°C caused marked decrease in the total conversions, which is a remarkable sign of significant retrogressive reactions. As pointed out in Song et al. [1989], the rate of coal thermal fragmentation is influenced by temperature and heating rate; very fast heating to high temperature would lead to extremely rapid fragmentation of coals that may exceed the capacity or rate of hydrogenation (H-donation) of the system, leading to significant retrogressive crosslinking. It is also likely that under SSL conditions (heating rates,  $\geq 100^\circ\text{C}/\text{min}$ ) very fast radical formation occurs before transformation of MoCo-TC2 into active phase is completed, resulting in an unbalance between the rate of radical formation and the rate of radical-capping by H from catalyst surface, especially at higher temperature. In TPL runs, however, the catalyst precursor decomposes to form active bimetallic sulfide and the weak linkages are broken and stabilized during programmed heat-up, so that at the time the radical formation becomes considerable at high temperature (425°C), the catalyst is already activated and can provide dissociated hydrogen atom to cap the thermally generated radicals. These mechanistic considerations account for why using MoCo-TC2 or TC3 affords further increased conversion and oil yield under TPL conditions but gives decreased conversion under SSL conditions when the final reaction temperature is increased from 400 to 425 °C.

In regards to the catalytic effects associated with solvent, the increases in conversion and oil yield due to catalyst are much higher when using a non-donor 1-MN solvent as compared to the runs using a H-donor tetralin (Table 4). For example, for SSL runs of DECS-9 coal at 400°C, using MoCo-TC2 increased coal conversion from about 32 to 75 wt% [(75-32)/32 = 134% increase] with 1-MN, and from about 71 to 88 wt% [(88-71)/71 = 24% increase] with tetralin. In the presence of H-donor solvent, the catalytic effects relative to thermal runs appear to be higher in SSL runs than under TPL conditions, as can be seen by comparing the thermal and catalytic runs with tetralin in Table 4.

## Conclusions

This work provides a fundamental approach to developing novel bimetallic dispersed catalysts and optimum conditions for coal conversion. We have synthesized and tested several heterometallic complexes consisting of two transition metals [Co, Mo] and sulfur as precursors of bimetallic dispersed catalysts for liquefaction of a subbituminous and a bituminous coal. The results revealed that both the ligands to the metal species and the type of bonding between the two metals affect the activity of the resulting catalyst significantly. Among the M-M" type precursors tested, Mo-Co thio cubane cluster,  $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp})_2(\text{CO})_2$  [MoCo-TC2], produced the best catalyst. Loading

of MoCo-TC2 at the level of 0.5 wt% Mo can increase the conversion of the subbituminous coal from 32 to as high as 80 wt%. The performance of the Mo-Co bimetallic catalyst was further enhanced by using temperature programmed heat-up (TPL) conditions. For a final temperature of 425°C, using the programmed conditions with MoCo-TC2 significantly increased the conversions by about 12-13 wt% for both coals, as compared to the non-programmed runs. Further work is now in progress.

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### References

- Brunner, H.; Wachter, J., *J. Organomet. Chem.* 1982, 240, C41-44.  
 Derbyshire, F.J.; *Catalysis in Coal Liquefaction*, IEACR/08, IEA Coal Research, London, 1988, 69 pp.  
 Garg, D.; Givens, E.N.; *Fuel Process. Technol.*, 1984, 8, 123-134.  
 Halbert, T. R.; Cohen, S. A.; Stieffel, E. I., *Organometallics* 1985, 4, 1689-1690.  
 Halbert, T.R.; Ho, T. C. Stieffel, E. I.; Chianelli, R. R., Daage, M., *J. Catal.* 1991, 130, 116-119.  
 Herrick, D. E.; Tierney, J. W.; Wender, I.; Huffamn, G. P.; Huggins, F. E., *Energy & Fuels* 1990, 4, 231-236.  
 Hirschon, A.S.; Wilson, R.B.; *Am. Chem. Soc. Sym. Ser.*, 1991, 461, 273-283.  
 Hirschon, A.S.; Wilson, R.B.; *Fuel*, 1992, 71, 1025-1031.  
 Huang, L.; Song, C.; Schobert, H. H., *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 1992, 37(1), 223-227.  
 Mingos, D.M.P.; Wales, D.J., "Introduction to Cluster Chemistry", Prentice Hall: Englewood Cliffs, New Jersey, 1990, 318 pp.  
 Solar, J.M.; Derbyshire, F.J.; de Beer, V.H.J.; Radovic, L.R.; *J. Catal.*, 1991, 129, 330-342.  
 Sommerfeld, D.A.; Jaturapitpornsakul, J.; Anderson, L.; Eyring, E.M.; *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 1992, 37(2), 749-755.  
 Song, C.; Nomura, M.; Miyake, M.; *Fuel*, 1986, 65, 922-926.  
 Song, C.; Hanaoka, K.; Nomura, M.; *Fuel*, 1989, 68, 287-292.  
 Song, C.; Nomura, M.; Ono, T., *Am. Chem. Soc. Div. Fuel Chem. Prepr.* 1991, 36(2), 586-596.  
 Song, C.; Schobert, H. H.; Hatcher, P. G., *Energy & Fuels*, 1992, 6, 326-328.  
 Song, C.; Schobert, H. H.; *Am. Chem. Soc. Div. Fuel Chem. Prepr.* 1992, 37(2), 976-983.  
 Suzuki, T.; Ando, T.; Watanabe, Y., *Energy & Fuels* 1987, 1, 299-300.  
 Swanson, A.; *Am. Chem. Soc. Div. Fuel Chem. Prepr.* 1992, 37(1), 149-155.  
 Yamada, O.; Suzuki, T.; Then, J.; Ando, T.; Watanabe, Y.; *Fuel Process. Technol.*, 1985, 11, 297-311.

**Table 1.** Liquefaction of DECS-9 Montana Subbituminous Coal at 400°C for 30 min

Catalyst precursor	Solvent for catalyst impregn <sup>a</sup>	Reaction solvent <sup>b</sup>	Reaction condition	Oil + Gas dmmf wt%	Asphalt dmmf wt%	Preasph. dmmf wt%	Tot Conv dmmf wt%
None	None	1-MN	SSL	16.0	9.4	6.8	32.2
MoCo-TC1	CH <sub>3</sub> CN	1-MN	SSL	22.8	4.8	5.2	32.8
MoCo-TC1	THF	1-MN	SSL	18.7	12.8	14.8	46.3
MoCo-TC2	Toluene	1-MN	SSL	32.4	18.0	24.2	74.6
MoCo-TC2	THF	1-MN	SSL	25.8	17.9	23.7	67.4
MoCo-TC3	Toluene	1-MN	TPL	33.8	17.8	19.9	71.5
MoCo-S	CHCl <sub>3</sub>	1-MN	SSL	21.3	12.6	16.0	49.8

a) The impregnating solvent was removed by evaporation in vacuum before reaction.

b) 1-MN was added as reaction solvent after the impregnating solvent was removed.

**Table 2.** Liquefaction of DECS-9 Montana Subbituminous Coal at 425°C for 30 min

Catalyst precursor	Solvent for catalyst impregn	Reaction solvent	Reaction condition	Oil + Gas dmmf wt%	Asphalt dmmf wt%	Preasph. dmmf wt%	Tot Conv dmmf wt%
None	None	1-MN	SSL	16.7	16.4	13.8	46.9
MoCo-TC1	THF	1-MN	SSL	20.3	9.9	5.7	35.9
MoCo-TC2	Toluene	1-MN	SSL	42.3	14.9	14.8	72.0
MoCo-TC2	THF	1-MN	SSL	36.5	15.5	18.0	70.0
MoCo-TC3	Toluene	1-MN	SSL	36.7	11.9	13.2	61.4
MoCo-S	CHCl <sub>3</sub>	1-MN	SSL	34.9	11.1	13.2	59.2

**Table 3.** Liquefaction of Pittsburgh #8 Bituminous Coal in 1-MN at 400-425°C

Catalyst precursor	Solvent for catalyst impregn	Reaction temp °C	Reaction condition	Oil + Gas dmmf wt%	Asphalt dmmf wt%	Preasph. dmmf wt%	Tot Conv dmmf wt%
None	None	400	SSL	13.7	20.4	26.8	60.9
MoCo-TC1	THF	400	TPL	9.8	21.9	34.0	65.7
MoCo-TC2	Toluene	400	SSL	14.5	27.8	34.3	76.6
None	None	425	SSL	16.2	19.1	16.1	51.4
MoCo-TC1	THF	425	TPL	16.9	24.6	19.4	60.8
MoCo-TC2	Toluene	425	SSL	21.8	27.7	23.8	73.3

**Table 4.** Effect of Temperature Programming on Coal Liquefaction Using Bimetallic Thiocubane Precursors MoCo-TC2 and MoCo-TC3\*\*

Catalyst precursor	Solvent for catalyst impregn	Reaction solvent	Reaction condition	Oil + Gas dmmf wt%	Asphalt dmmf wt%	Preasph. dmmf wt%	Tot Conv dmmf wt%
<b>DECS-9 Montana Subbit Coal</b>							
None	400	1-MN	SSL	16.0	9.4	6.8	32.2
None	400	1-MN	TPL	18.9	8.2	7.0	34.1
MoCo-TC2	400	1-MN	SSL	32.4	18.0	24.2	74.6
MoCo-TC2	400	1-MN	TPL	37.0	19.8	22.0	78.7
None	425	1-MN	SSL	16.7	16.4	13.8	46.9
MoCo-TC2	425	1-MN	SSL	42.3	14.9	14.8	72.0
MoCo-TC2	425	1-MN	TPL	46.7	19.5	15.0	81.1
MoCo-TC3	425	1-MN	SSL	36.7	11.9	13.2	61.4
MoCo-TC3	425	1-MN	TPL	46.3	17.5	12.9	76.6
None	400	Tetralin	SSL	29.4	20.6	21.4	71.4
None	400	Tetralin	TPL	34.4	21.1	23.7	79.2
MoCo-TC2	400	Tetralin	SSL	44.1	22.9	21.0	88.1
MoCo-TC2	400	Tetralin	TPL	46.4	25.4	17.4	89.2
<b>DECS-12 Pittsburgh #8 Bitum Coal</b>							
None	400	1-MN	SSL	13.7	20.4	26.8	60.9
MoCo-TC2	400	1-MN	SSL	14.5	27.8	34.3	76.6
MoCo-TC2	400	1-MN	TPL	15.8	28.7	35.4	79.9
None	425	1-MN	SSL	16.3	17.6	16.1	51.4
MoCo-TC2	425	1-MN	SSL	21.8	27.6	23.9	73.3
MoCo-TC2	425	1-MN	TPL	33.1	31.5	23.4	87.9
MoCo-TC2	400	Tetralin	SSL	18.8	32.6	31.0	82.4
MoCo-TC2	400	Tetralin	TPL	21.9	34.2	33.0	89.1

\*\* Impregnated from toluene solution using incipient wetness method.